CHAPTER VII

TECHNO-ECONOMIC COMPARISON OF ENERGY USAGE BETWEEN AZEOTROPIC DISTILLATION AND HYBRID SYSTEM FOR WATER–ETHANOL SEPARATION

7.1 Abstract

Conventional azeotropic distillation, consuming very high energy, is mostly used to produce high purity ethanol for renewable energy usage. In this study, the techno-economic comparison between azeotropic distillation (distillation followed by practical azeotropic distillation) and hybrid system (distillation followed by pervaporation system) for producing high purity of ethanol is demonstrated using the Pro II by Provision version 8.0. In the hybrid system, NaA zeolite membrane is used to separate the water from ethanol-water mixture. It is found that the hybrid system is the most effective technique for producing more than 99.4 %wt of ethanol with an energy consumption of 52.4% less than the azeotropic distillation.

7.2 Introduction

Although the most widely used technique to produce ethanol is the distillation process, it can only produce ethanol with a purity close to 95 %wt owing to the formation of the azeotropic phase between water and ethanol [1-2]. The azeotropic distillation, involving the additional component called "entrainer" to separate water from ethanol by distillation [3], was thus introduced to solve this problem. However, azeotropic distillation is not only an energy-consuming process, but is also environmentally unfriendly, due to the toxicity of the entrainer used [4-5]. Pervaporation technique is the technique used to solve these problems because it consumes less energy and is more environmentally friendly [5-6]. The separation of this technique depends on the diffusion coefficient and relative affinity of each component in a membrane [2, 7]. By applying vacuum at the permeate side, it creates a driving force across the membrane to separate one component from the mixture.

This technique can overcome the azeotropic composition problem found in the distillation process.

Membranes used in the pervaporation system are polymeric, inorganic or ceramic, and mixed-matrix membranes, depending on particular applications [8-11]. Sodium A zeolite membrane is a good candidate for water-ethanol separation using the pervaporation system [10, 12] since water can more easily pass through the membrane and go to the permeate side due to the hydrophilicity of the membrane, resulting in higher purity of ethanol in the retentate side.

Although a hybrid system — the distillation process followed by the pervaporation technique — has proven to be a better way to produce high purity ethanol (higher than 99.5%wt), the techno-economic analysis of this system has not yet been studied. In this article, the techno-economic analysis of the azeotropic distillation using benzene or cyclohexane as an entrainer was explored, comparing it to the hybrid system using the software called PRO II by Provision version 8.0 as a simulation program. Lab-scale pervaporation system of water-ethanol separation using our home-made NaA zeolite membrane was introduced to collect data and simulate the hybrid system.

7.3 Experimental

7.3.1 Materials

Fumed silicon dioxide (SiO_2, $390\pm40m^2/g$ surface area, 0.007 μm average particle size) and aluminum hydroxide hydrate [$Al(OH)_3.xH_2O$, 51 m^2/g surface area] were purchased from Sigma-Aldrich, Inc., and were used as starting materials. Sodium hydroxide (NaOH), from Lab-Scan Analytical Sciences, was used as a base catalyst. Ethyl alcohol (ethanol, UN 1170, 99.5%) was purchased from J.T. Baker Solusorb. The tubular porous α-alumina support obtained from the National (Thailand) Metal and Materials Technology Center (MTEC), having an 11 mm O.D., a 9 mm I.D., a 6 cm length, and a 0.3 μm pore radius on average with 38% porosity,

and coated with an α-alumina intermediate (0.06 μm pore size) on the top layer, was used in this work.

7.3.2 NaA zeolite membrane synthesis

The synthesis followed those reported elsewhere [12-14]. A tubular porous alumina support was cleaned by washing twice in deionized water for 15 min to remove dirt from the surface, dried in a vacuum oven at 363 K for 24 h, and calcined in a furnace at 400 K for 3 h to burn off any impurities from its surface. The unsoiled tubular alumina support was placed in a vacuum seeding system, containing the NaA seed crystal solution, for 2 min at 10 mmHg (1.333 kPa), followed by drying at 60 K for 24 h before coating with NaA zeolite autoclave technique. The NaA seed crystal solution was prepared by dispersing about 7 g of NaA zeolite (0.5 μm pore size an average) in 1000 mL of water. The NaA zeolite seed was synthesized using the formula composition as follows: $3Na_2O$: Al_2O_3: SiO_2: $410H_2O$ [7,13,15].

The coated tubular support was placed in a teflon vessel containing the NaA zeolite solution prepared using the $50Na_2O$: Al_2O_3: $5SiO_2$: $1000H_2O$ formula. The vessel was then equipped in the autoclave machine and placed in the vacuum oven at 333k for 20 h to obtain the NaA zeolite membrane. The membranes were washed with deionized water and dried at 343 K for 24 h before pervaporation testing.

7.3.3 Pervaporation experiment

The pervaporation system was kept constant at 343 K. A circulation pump (Masterflex) was used to pump the water-ethanol ratio of 10:90 with the 510 mL total amount of throughput from the heat tank to the pervaporation unit. The permeate was collected in the vessel, cooled by using the liquid nitrogen, to calculate the total water flux $(kg/m^2/h)$ and the separation factor (dimensionless). An EDWARDS LS63P vacuum pump equipped with the pervaporation unit was used at the permeate side and kept pressure constant at 10 mmHg.

The total water flux and the separation factor were used to determine the performance of the synthesized NaA zeolite membrane in pervaporation units, calculated by using eq. I and II;

$$\text{Total water flux (J)} \quad = \quad W / [A*t] \quad\quad\quad (I)$$

where W is the water permeate (kg), A is the membrane area (m^2), and t is time (h). In this work, the total water flux was determined when the time was varied in the recycle-continuous pervaporation testing.

$$\text{Separation factor } (\alpha) \quad = \quad \left[X_{EtOH} / X_{H_2O} \right]_{perm} / \left[X_{EtOH} / X_{H_2O} \right]_{reten} \quad\quad (II)$$

where X_{EtOH} and   are the molar fractions of ethanol and water, respectively. The subscripts of perm and reten represent the permeate and the retentate sides, respectively.

7.3.4 Sample Analysis

The separated water–ethanol products were analyzed using an Agilent Technologies 6890N gas chromatograph equipped with an HP-Plot/Q capillary column and a TCD detector. About 0.5 μL of the samples was injected under the following conditions: the helium used as the carrier gas was set at 55 kPa, the oven temperature was set at 473K, while the injector and detector temperatures were set at 473K and 523K, respectively.

7.3.5 Simulation programs

To compare the processes between the azeotropic distillation system and the hybrid system, we assumed that 1000 kg/h of water-ethanol mixture (50%wt of ethanol and 50%wt of water) was used as a feedstock to produce 99.5% ethanol. The temperature and the pressure of the initial feedstock were set at 298 K, 1 atm for the azeotropic distillation system and 343K, 1 atm for the pervaporation unit in the hybrid system. For the practical azeotropic distillation system, distillation column

followed by azeotropic distillation was used to produce 99.5% ethanol. For the hybrid system, the distillation column followed by the pervaporation system, using NaA zeolite membrane, was used to produce 99.5% ethanol. The first distillation column for both systems was the same, thus, a comparison between the pervaporation and the practical azeotropic distillation systems was studied for comparison in term of techno-economics for 99.5%wt of ethanol production.

For simulating both systems, Pro II with PROVISION version 8.0 was used to obtain the total amount of energy required for purification of ethanol to reach 99.5%wt of ethanol, total ethanol production rate, total stage of each distillation column, and total amount of membrane surface area for the pervaporation system. Moreover, in the azeotropic distillation system, since benzene and cyclohexane were used as an entrainer to purify ethanol from 94 to 99.5 %wt, a comparison between benzene and cyclohexane was also studied in term of energy and production points of view.

7.4 Results and discussion

7.4.1 Pervaporation testing results

As can be seen in Fig. 7.1 and Table 7.1, to reach 99.5%wt of ethanol, the lab-scale pervaporation system for water-ethanol separation using our home-made NaA zeolite membrane showed an impressive performance with the total water flux as high as 2.12 $kg/m^2/h$ and the separation factor higher than 10,000 for all membranes tested and all water-ethanol mixtures in the ranges from 90–95% (below the azeotropic point) and 95–99.5% (above the azeotropic point).

7.4.2 Simulation program

For simulating the azeotropic distillation (distillation column followed by practical azeotropic distillation column) and the hybrid (distillation column followed

by pervaporation unit) systems using the PRO II program, the feed flow rate was assumed as 1,000 kg/h with 50:50 ethanol:water at atmospheric pressure. 298 K was employed as the initial feed temperature before moving to the distillation column of both systems to reduce the energy consumption of the distillation process. The temperature of the practical azeotropic distillation column of the azeotropic distillation system was set at 351 K, while that of the pervaporation unit of the hybrid system was set at 343 K, which is the same as the one set in the lab scale pervaporation testing.

7.4.2.1 Distillation column

Ethanol-water mixture with the %wt ratio of 50:50 was first purified in the distillation column to obtain a higher purity of ethanol. Total distillation column stages of 20 at the stage number 18 and the reflux ratio (R) of 20 was acquired from the simulation program, as shown in Fig. 7.2. The feed rate of the ethanol mixture produced from this process was 531.84 kg/h with 94 %wt with 6 %wt of water which is close to the azeotropic composition of water and ethanol (around 95:5 %wt of ethanol:water) [3, 16]. That means that other techniques are needed to combine with the distillation column to increase the purity of ethanol.

7.4.2.2 Azeotropic distillation

A result of the azeotropic distillation from the PRO II simulation program, requiring 25 stages of practical azeotropic distillation column with the reflux ratio of 20, is shown in Fig. 7.3. The 531.84 kg/h of the product feed rate with a composition close to azeotropic point of ethanol obtained from the distillation column was moved to the practical azeotropic distillation column, using benzene (or cyclohexane) as an entrainer fed from the top of the column. The azeotropic mixture stream was fed from the bottom at stage 23. The entrainer can break the azeotropic mixture (water-ethanol azeotrope), resulting in a very high purity of ethanol (as high as 99 %wt of ethanol with the feed flow rate of 504.97 kg/h). However, the final specification of

the required ethanol for industry is at least 99.5%wt of ethanol; thus, the addition of the second practical azeotropic distillation column, using the same conditions as the first one, was introduced in the system, as can be seen in Table 7.2. The purity of the ethanol produced was increased, but still contained less than 99.5%wt of ethanol. The addition of the third practical azeotropic distillation column was thus conducted, causing higher investment, operation, and energy costs, as stated in Hoof et al. [2] who also found that total cost increased with a rise in the capacity and the amount of azeotropic distillation column.

In addition, changing the type of the entrainer from benzene to cyclohexane, as shown in Fig. 7.4, indicated that 3 kg/h of cyclohexane, higher than benzene, was required to produce 99 %wt of ethanol, as shown in the figure, implying that benzene was more effective than cyclohexane for purifying the ethanol in this simulation program.

7.4.2.3 Hybrid system (distillation followed by pervaporation system)

The hybrid system studied in this work is shown in Fig. 7.5. The first distillation column was the same as that used in the azeotropic distillation process, meaning that the starting feed stream for the pervaporation system was 531.84 kg/h, having the composition of 94 %wt of ethanol and 6 %wt of water. From the simulation program, it was found that 15 m^2 surface area of the NaA zeolite membrane was required to produce 99.5%wt of ethanol with the ethanol amount of 502.44 kg/h.

7.4.3 Techno economic calculations

In this work, we consider the total energy required to produce 99.5 %wt of ethanol, examining not only both the azeotropic distillation and the hybrid systems, but also the type of entrainer, benzene and cyclohexane. To compare the cost of the operation for both systems, the energy required for the practical azeotropic distillation was compared to that required for the pervaporation system, as

summarized in Table 7.3. The pervaporation system consumed less energy to produce 99.5%wt of ethanol; hence the whole mixture was not needed to distill, as compared to the azeotropic distillation system, which requires the addition of the second and the third azeotropic columns. In the pervaporation system, only the permeating component, which is pure water, required a heat of evaporation, as mentioned by Hoof *et al.* [2], who also found that the energy required for water evaporation in the pervaporation system was lower than that in the azeotropic distillation system. Furthermore, even though the energy required (Q_R) for producing ethanol by using cyclohexane was slightly lower than benzene, the amount of cyclohexane required for purifying ethanol to 99 %wt was higher, as can be seen in Table 7.4. From this point, we may infer that benzene was a more effective entrainer than cyclohexane for using as an entrainer in the practical azeotropic distillation.

Commercially, the energy required to produce 99.5%wt ethanol was expressed in terms of condenser energy required (Q_C) and reboiler energy required (Q_R) in the distillation and the practical azeotropic distillation columns. Thus, considering the cost of each system in the purification of ethanol, it was assumed that both of Q_C and Q_R were come from electric energy needed and used to calculate the total cost of the operation of each system. However, the important value in the process was the supplied heat (Q_R) to produce ethanol. Rejecting the heat to environment is not expensive, as long as it can reject at ambient temperature. Thus, the total energy required and calculated comes from the energy required (Q_R) for producing ethanol and the total energy (Q_R+Q_C) for producing ethanol.

The electricity cost used in the calculation using the techno-economics analysis was 35€/MW.h, as used in the study of Hoof *et al.* [2]; thus, the cost of the total energy required and the cost of the total energy of each system were determined, as shown in Tables 7.5 and 7.6. The azeotropic distillation system (distillation followed by practical azeotropic distillation) consumed 54% more energy than the pervaporation system, resulting in a very high energy cost, consistent with the results found by Hoof *et al.* [2]. Furthermore, although the azeotropic distillation system, consisting of the second and the third practical azeotropic distillation columns, could produce high purity of the ethanol, the operating cost was

remarkably high. In other words, the addition of the practical azeotropic distillation column in the distillation system was not good in terms of a techno-economics view.

As a result, the hybrid system of distillation column followed by a pervaporation system using our home-made NaA zeolite membrane was the best system for producing ethanol at very high purity (higher than 99.5%wt) at much lower cost.

7.5 Conclusions

Using a techno-economics analysis, the hybrid process system using NaA zeolite membrane was more economically attractive than the azeotropic distillation process system. It not only saved significant energy required for producing 99.5 %wt of ethanol, but was also an environmentally friendly process. For the azeotropic distillation system, benzene was a better entrainer than cyclohexane in term of investment cost. Moreover, using the data obtained from the laboratory scale for the pervaporation system carried out using NaA zeolite membrane, the results from a simulation provided a good performance for the water-ethanol separation. We may conclude that the combination of this system and a distillation was suitable and efficient in term of techno-economic analysis for the ethanol production.

7.6 Acknowledgements

7.7 References

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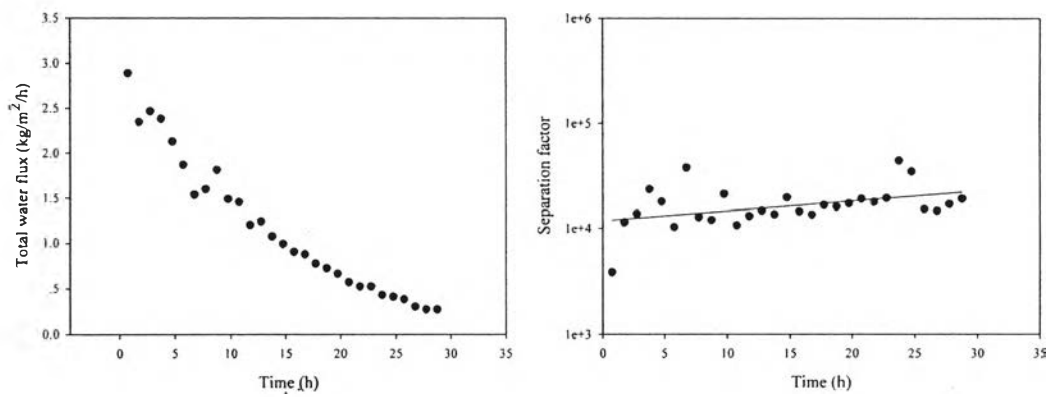16. A. Verhoef, J. Degreve, B. Huybrechs, H. van Veen, P. Pex and B.V. der Bruggen, *Comput. Chem. Eng.*, 32, 1135-1146 (**2008**).

Figure 7.1 Total water flux (kg/m²/h) and separation factor of the pervaporation system using NaA zeolite membrane.
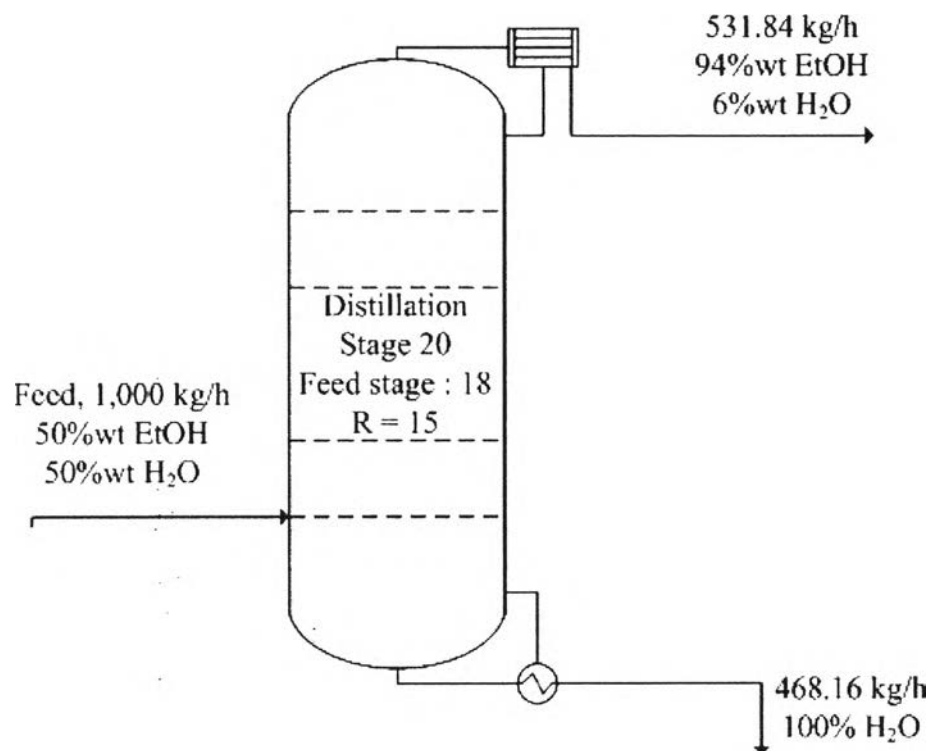
Figure 7.2 Ethanol purification in the distillation column using PRO II simulation program.

Figure 7.3 Azeotropic distillation system (distillation column followed by practical azeotropic distillation column) using benzene (Ben) as an entrainer.
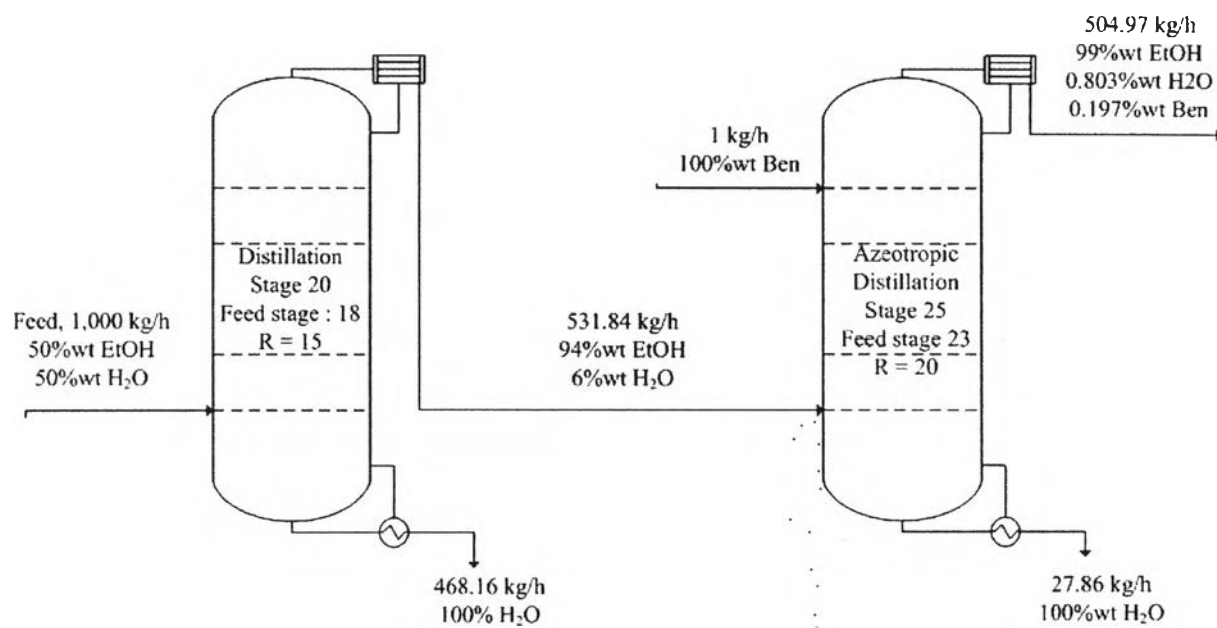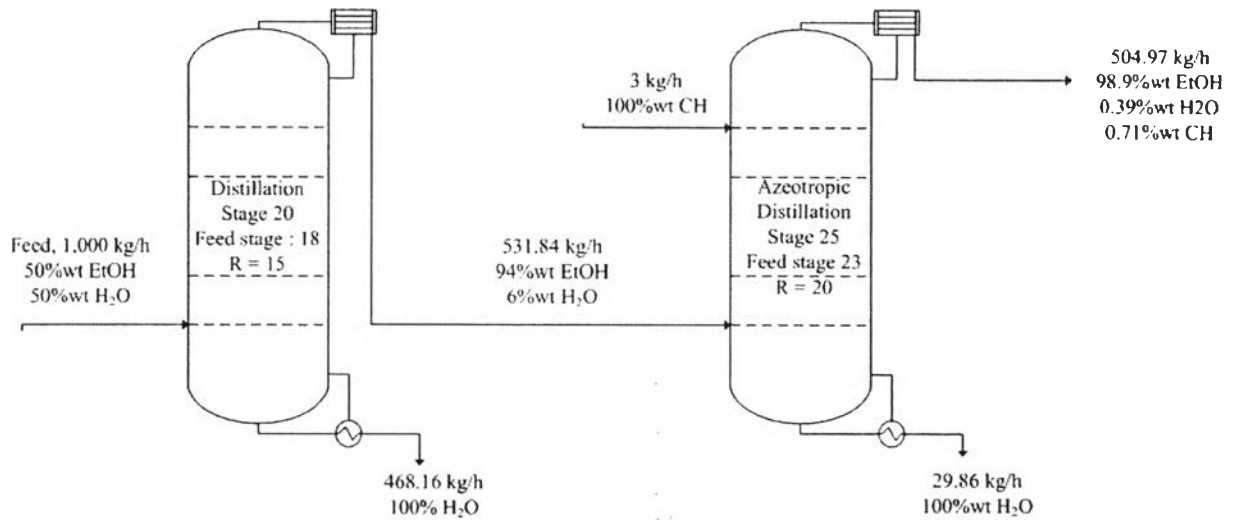
Figure 7.4 Azeotropic distillation system (distillation column followed by practical azeotropic distillation column) using cyclohexane (CH) as an entrainer.
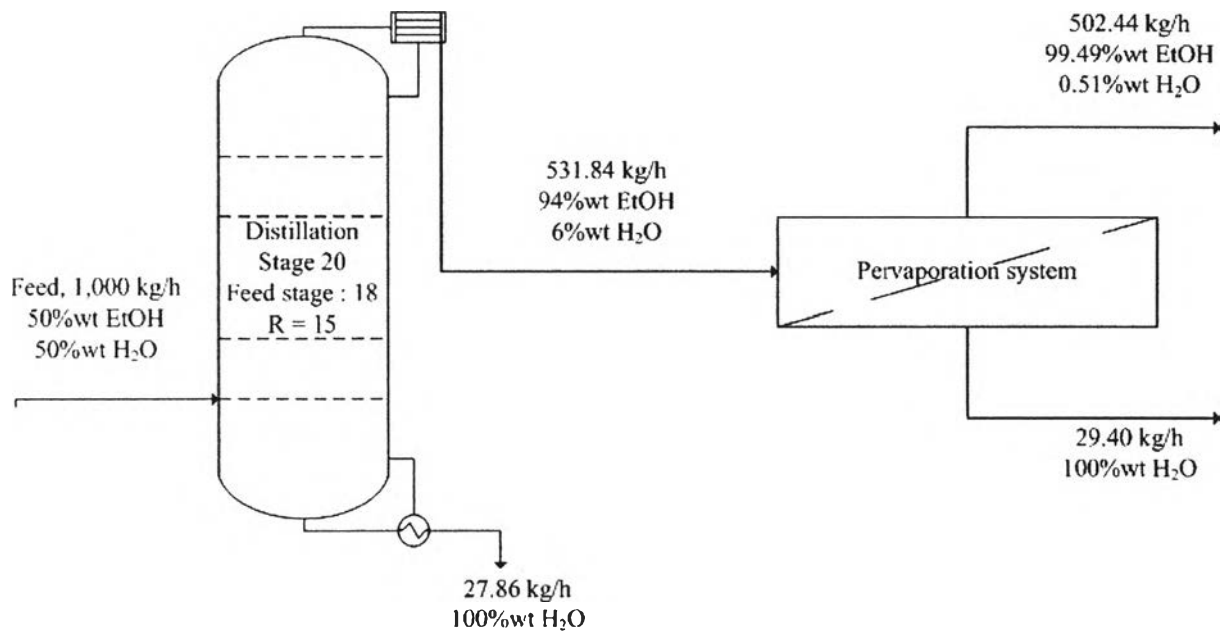
Figure 7.5 Schematic diagram of the hybrid system, composing of distillation column and pervaporation system.

Table 7.1 Performances of synthesized NaA zeolite membrane in lab scale pervaporation system for water-ethanol separation.

% Ethanol feedstock	Final % ethanol	Average total water flux $(kg/m^2/h)$	Average separation factor	Time (h)
90	95	2.12	> 10,000	8.75
95	99.5	0.76	> 10,000	20

Table 7.2 Data obtained from simulation program of distillation column followed by azeotropic distillation column to produce 99.5 %wt ethanol.

Column	Inlet feed flow rate (kg/h)	Inlet feed composition (%EtOH:%H$_2$O:%Entrainer)	Product stream flow rate (kg/h)	Product composition (%EtOH:%H$_2$O:%Entrainer)
Distillation	1,000	50: 50	531.84	94: 6
1st Azeotropic distillation	531.84	94: 6	504.97	99: 0.803: 0.197(Bz)
2nd Azeotropic distillation	504.97	99: 0.803: 0.197 (Bz)	503.60	99.26: 0.39: 0.35(Bz)
3rd Azeotropic distillation	503.60	99.26: 0.39: 0.35 (Bz)	502.89	99.33: 0.156: 0.514(Bz)

Table 7.3 Total energy required for each process to produce high purity of ethanol.

Technique	Energy required: (MJ/kg ethanol)										%Ethanol product (%wt)
	Distillaiton column		1st Practical azeotropic		2nd Practical azeotropic		3rd Practical azeotropic		Total Energy required	Pervaporation system	
	$Q_C^{\bullet}$	$Q_R^{\bullet\bullet}$	Q_C	Q_R	Q_C	Q_R	Q_C	Q_R			
Distillation	7.96	8.18	-		-	-	-	-	16.14	-	94
Azeotropic distillation[a]	7.96	8.18	10.14	10.02	-	-	-	-	36.30	-	99
Azeotropic distillation[b]	7.96	8.18	10.14	10.02	10.31	9.79	-	-	56.40	-	99.26
Azeotropic distillation[c]	7.96	8.18	10.14	10.02	10.31	9.79	10.25	9.74	76.39	-	99.33
Hybrid system	7.96	8.18	-		-	-	-	-	16.14	1.134	99.50

$^{\bullet}Q_C$ = Condenser energy required, $^{\bullet\bullet}Q_R$ = Reboiler energy required

[a] distillation column followed one practical azeotropic distillation, [b] distillation column followed two practical azeotropic distillation,

[c] distillation column followed three practical azeotropic distillation.

Table 7.4 Practical azeotropic distillation using different types of entrainer.

Entrainer	Total amount required (kg/h)	Final %wt ethanol produced	Total amount of ethanol produced (kg/h)	Energy required (MJ/kg)	
				Q_C	Q_R
Benzene (Ben)	1	99.00	504.98	10.14	10.02
Cyclohexane (CH)	3	98.90	504.97	10.076	9.958

Table 7.5 Cost of operating energy required (Q_R) for each system.

Technique	Total energy required : Q_R (MJ/kg ethanol)					Total energy required (MJ/kg)	Total cost of operation system (€/kg)
	Distillation column	1st Practical azeotropic	2nd Practical azeotropic	3rd Practical azeotropic	Pervaporation system		
Distillation	8.18	-	-	-	-	8.18	0.0794
Azeotropic distillation[a]	8.18	10.02	-	-	-	18.20	0.1771
Azeotropic distillation[b]	8.18	10.02	9.79	-	-	27.99	0.2723
Azeotropic distillation[c]	8.18	10.02	9.79	9.74	-	37.73	0.3675
Hybrid system	8.18	-	-	-	1.134	9.314	0.0906

Table 7.6 Cost of total operating energy ($Q_R + Q_C$) for each system.

Technique	Total energy for Producing Ethanol : Q_C+Q_R (MJ/kg ethanol)					Total energy required (MJ/kg)	Total cost of operation system (€/kg)
	Distillation column	1st Practical azeotropic	2nd Practical azeotropic	3rd Practical azeotropic	Pervaporation system		
Distillation	16.14	-	-	-	-	16.14	0.1568
Azeotropic distillation[a]	16.14	20.16	-	-	-	36.30	0.350
Azeotropic distillation[b]	16.14	20.16	20.10	-	-	56.40	0.5495
Azeotropic distillation[c]	16.14	20.16	20.10	19.99	-	76.39	0.742
Hybrid system	16.14	-	-	-	1.134	17.274	0.168